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Chemical and Structural Relationships Among the Oligomeric Compounds
$MFe(CO)_4$ (M=Zn, Cd, Hg), $PbFe(CO)_4$, $AgCo(CO)_4$, and Their Lewis Base Adducts.

by

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Evanston, Illinois 60201

CHEMICAL AND STRUCTURAL RELATIONSHIPS AMONG
THE OLIGOMERIC COMPOUNDS $MFe(CO)_4$ (M = Zn, Cd, Hg),
$PbFe(CO)_4$, $AgCo(CO)_4$, AND THEIR LEWIS BASE ADDUCTS.

by Richard D. Ernst[1] and Tobin J. Marks[*2]

ABSTRACT

The synthesis and characterization of the following new metal-metal bonded com-
plexes are reported: $(pyridine)_3ZnFe(CO)_4$, $(NH_3)(2,2'-bipyridyl)ZnFe(CO)_4$, $(2,2':$
$6,2''-terpyridyl)CdFe(CO)_4$, $(2,2',2''-triaminotriethylamine)CdFe(CO)_4$, $(2,2'-$
$bipyridyl)ZnFe(CO)_4$, $(4,4'-bipyridyl)CdFe(CO)_4$, and $(4-phenylpyridine)CdFe(CO)_4$.
Proper ligational strategy thus allows the isolation of several types of compounds
which differ from the previously known $B_2CdFe(CO)_4$ and $(NH_3)_3ZnFe(CO)_4$ patterns.
It is also possible to manipulate the degree of association of these species by con-
trol of the group IIb metal ion coordination sphere. Thus the first four of the new
compounds listed are tentatively assigned monomeric structures, while the latter
three are assigned oligomeric structures. The present studies also reveal that
$AgCo(CO)_4$ is isomorphous with $[CdFe(CO)_4]_4$, and that $(pyridine)_2CdFe(CO)_4$
exists as a trimer in the solid state. The complex $(2,2'-bipyridyl)AgCo(CO)_4$ is
found to be partly associated in noncoordinating solvents. In the solid state, $PbFe(CO)_4$
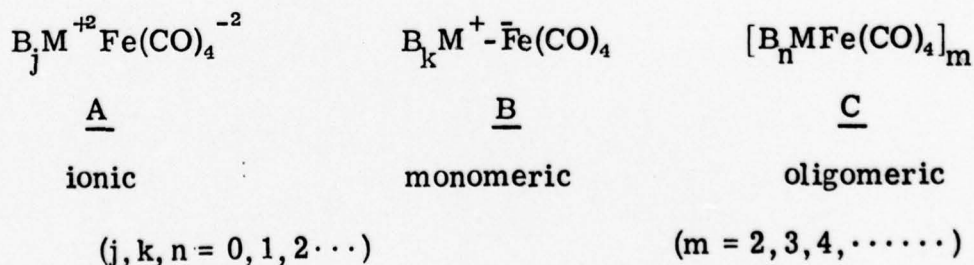is associated.

It has been known for some time that the metal-metal bonded oligomer $[CdFe(CO)_4]_n$[3] forms adducts, $B_2CdFe(CO)_4$, with a wide variety of Lewis bases, B.[3,4] Until very recently there has been no structural information available for any of these materials. Diffraction studies have now shown that $[CdFe(CO)_4]_n$ is a tetramer with approximately D_{4h} symmetry[5a] and that $(2,2'-bpy)CdFe(CO)_4$, bpy = bipyridyl, is a trimer with approximately D_{3h} symmetry.[5b] The molecular geometries of these compounds are illustrated in Figure 1. The structures of $CdFe(CO)_4$ adducts with other Lewis bases remain largely undefined. The compound $[HgFe(CO)_4]_4$ is also known[6,7] and is isomorphous with $[CdFe(CO)_4]_4$,[5a] but no base adducts have been isolated. In comparison to the results for cadmium and mercury, the only reported zinc-containing derivative, $B_3ZnFe(CO)_4$ where $B = NH_3$,[7] contains three molecules of base. Unlike the cadmium diammine, $(NH_3)_2CdFe(CO)_4$, the zinc triammine does not readily lose ammonia on heating in vacuo.[4] A number of structural types are conceivable for the above Lewis base adducts, viz. A - C. In isoelectronic group Ib metal-transition metal carbonyl chemistry

$$B_jM^{+2}Fe(CO)_4^{-2} \qquad B_kM^{+}-\bar{\bar{F}}e(CO)_4 \qquad [B_nMFe(CO)_4]_m$$

A	B	C
ionic	monomeric	oligomeric
$(j, k, n = 0, 1, 2 \cdots)$		$(m = 2, 3, 4, \cdots\cdots)$

$$M = Zn, \ Cd, \ Hg$$

an analogous range of possibilities exists for the compounds $AgCo(CO)_4$, and $B_nAgCo(CO)_4$.[8] Likewise, little is known about the related group IVb derivative $PbFe(CO)_4$.[9]

From the above discussion it can be seen that the relationships between stable oligomeric structures as well as allowed structural interconversions in group IIb and Ib metal-transition metal compounds depend on ligands and metals in a way that has not been investigated in depth. The details of, and reasons for, such relationships are of importance to studies of metal-metal bonding in general and to the challenge of preparing infinite metal atoms arrays in particular. In this article we report on the synthesis of several new types of group IIb metal-transition metal complexes and discuss, on the basis of physical measurements, possible chemical and structural relationships in the $B_nMFe(CO)_4$ (M = Zn, Cd, Hg), $AgCo(CO)_4$, $B_nAgCo(CO)_4$, and $PbFe(CO)_4$ classes of molecules.

EXPERIMENTAL

All operations involving metal carbonyls were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glove box. Solvents were thoroughly dried and deoxygenated in a manner appropriate to each, and were distilled under nitrogen immediately prior to use. Elemental analyses were performed by Miss H. Beck, Northwestern University Analytical Services Laboratory, Dornis and Kolbe Analytical Laboratories, or Schwarzkopf Analytical Laboratories. Osmometric molecular weight determinations were also carried out by Miss H. Beck using a Mecrolab Model 302 instrument.

Mercurytetracarbonyliron, $HgFe(CO)_4$. This compound was prepared by the procedure of Brauer,[10] and was dried overnight under high vacuum. The infrared spectrum of a Nujol mull was identical with that reported previously.[11]

Thalliumtetracarbonylcobalt, $TlCo(CO)_4$. This was prepared from thallium metal and $Co_2(CO)_8$ as described by Robinson et al.[12a] The infrared spectral parameters were identical to those previously reported,[12b] and are consistent with the essentially ionic structure found by x-ray structural determination[12a].

Leadtetracarbonyliron, $PbFe(CO)_4$. This very air-sensitive black compound was prepared by the method of Krumholz and Bril.[9]

Diamminecadmiumtetracarbonyliron, $(NH_3)_2CdFe(CO)_4$. This compound was synthesized by the procedure of Feigl and Krumholz,[3] and was dried overnight under high vacuum. Infrared spectral parameters were identical with those previously reported.[5a]

Cadmiumtetracarbonyliron, $CdFe(CO)_4$ and bis(pyridine)cadmium tetracarbonyliron, $(py)_2CdFe(CO)_4$. These were prepared from $(NH_3)_2$-$CdFe(CO)_4$ according to our previous procedures.[5a]

(2,2',2''-triaminotriethylamine)cadmiumtetracarbonyliron, (tren)CdFe-$(CO)_4$. To a suspension of 1.40 grams (4.45 mmoles) of $(NH_3)_2CdFe(CO)_4$ in 40 ml diethylether under nitrogen was added an excess (1.0 ml) of 2,2',2''-triaminotriethylamine with stirring. After three hours, stirring was discontinued and the solid product was allowed to settle. The supernatant was removed, the product was washed three times with 25 ml portions of diethylether, and dried in vacuo overnight. The compound is only very slightly soluble in most organic solvents. Crystalline material could best be obtained by a controlled ligand replacement in which a solution of 2,2',2''- triaminotriethylamine is slowly reacted with (2,2'-bpy) $CdFe(CO)_4$.[5]

Anal. Calcd. for $C_{10}H_{18}CdFeN_4O_4$: C, 28.16; H, 4.25; N, 13.14. Found: C, 27.84; H, 4.31; N, 12.93.

Complete infrared data (Nujol mull): 3364m, 3310w, 3212m, 3126sh, 1948s, 1857s, 1815sh, 1798vs, br, 1583s, 1314m, 1268w, 1107w, 1094w, 1065s, 1037s, 1000m, 973m, 883m, 855w, 734w, 716w, 626s cm^{-1}.

Attempted preparation of bis(2, 2'-bipyridyl)cadmiumtetracarbonyliron, (2, 2'-bpy)$_2$CdFe(CO)$_4$. To 50 ml of deoxygenated aqueous ammonia was added 1.3 ml of Fe(CO)$_5$ (0.010 moles) under nitrogen and the resulting mixture was stirred overnight. To this solution of HFe(CO)$_4^-$ was added 50 ml of deoxygenated aqueous solution containing 2.67 grams (0.01 moles) of cadmium acetate dihydrate and 3.12 grams (0.02 moles) of 2-2' bipyridine at 0° C. This resulted in the precipitation of a yellow-orange solid which was filtered, washed with three 20 ml portions of deoxygenated water followed by three 20 ml portions of diethylether, and dried in vacuo. Elemental analysis (C, H, N), infrared spectroscopy, and x-ray powder diffraction identified the product as [(2, 2'-bpy)CdFe(CO)$_4$]$_3$.[5]

(2, 2'-6', 2''-terpyridyl)cadmiumtetracarbonyliron, (tpy)CdFe(CO)$_4$. A slight excess of 2, 2': 6', 2''-terpyridine (0.20 grams, 0.86 mmoles) was dissolved in 10 ml acetone and added dropwise to 0.20 grams (0.71 mmoles) of CdFe(CO)$_4$ in 25 ml acetone under nitrogen with stirring. A reddish-orange precipitate immediately formed, and after two hours of stirring, the supernatant was removed. The solid product was then washed with three 25 ml portions of acetone, and dried in vacuo. The product so obtained smolders in air and is nearly insoluble in most organic solvents, except pyridine. Crystalline materials, significantly more air-resistant, may be obtained by slow diffusion of the reacting species through a medium glass frit.

<u>Anal</u>.[13] Calcd. for $C_{19}H_{11}CdFeN_3O_4$: C, 44.44; H, 2.16; N, 8.18, Cd, 21.89; Fe, 10.87. Found: C, 42.30; H, 2.48; N, 8.59, Cd, 22.32; Fe 11.20.

Complete infrared data (Nujol mull): 1985sh, 1973s, 1887s, 1872sh, 1850sh, 1593m, 1579w, 1573w, 1563w, 1433sh, 1419sh, 1306w, 1241w, 1186w, 1162w, 1155w, 998w, 754s, 645m, 622s cm^{-1}.

<u>(4,4'-bipyridyl)cadmiumtetracarbonyliron, (4,4'-bpy)CdFe(CO)$_4$.</u> This compound was prepared by stirring stoichiometric amounts of 4,4'-bipyridyl dihydrate (0.50 grams, 2.6 mmoles) and CdFe(CO)$_4$ (0.73 grams, 2.6 mmoles) in 30 ml acetone under nitrogen for one day. The bright yellow precipitate which had formed immediately was then filtered from the supernatant, washed with several 10 ml portions of acetone, followed by several 20 ml portions of ether, and dried <u>in vacuo</u>.

<u>Anal</u>. Calcd. for $C_{14}H_8CdFeN_2O_4$: C, 38.52; H, 1.86; N, 6.42. Found: C, 37.83; H, 1.58; N, 6.03.

Complete infrared data (Nujol mull): 1977s, 1904s, 1892s, sh, 1604m, 1534w, 1491sh, 1414m, 1317w, 1219m, 1215m, 1062m, 1042w, 997m, 847w, 799m, 606s cm^{-1}.

<u>(4-phenylpyridine)cadmiumtetracarbonyliron, (4-$C_6H_5C_5H_4N$)CdFe(CO)$_4$.</u> To 0.33 grams (1.18 mmoles) of CdFe(CO)$_4$ in 30 ml acetone at -78°C under nitrogen was added 0.15 grams (0.97 mmoles) of 4-phenylpyridine with stirring. The solution was allowed to reach room temperature over a period of several hours, and was then stirred two more hours. The volume of the solution was next reduced by one-half, 50 ml pentane was added, and the solution cooled to -78°C, producing a yellow mixture

of crystals and micro-crystalline powder. The supernatant was removed, the solid was washed twice with 20 ml portions of diethylether, and thoroughly dried in vacuo. The product was next taken up in a minimum volume of methylene chloride, and filtered from any residue (unreacted $CdFe(CO)_4$). An equal volume of pentane was added to the filtrate at -78°C, producing a beautiful lemon-yellow micro-crystalline solid. After removal of solvent, the somewhat air-sensitive product was dried in vacuo for one hour.

Anal.: Calcd. for $C_{15}H_{10}CdFeNO_4$: C, 41.28; H, 2.31; N, 3.21. Found: C, 40.87; H, 2.31; N, 3.33.

Complete infrared data (Nujol mull): 2000s, 1990sh, 1941sh, 1933sh, 1914s, 1907sh, 1891s, 1868sh, 1840m, 1806m, 1606m, 1546w, 1483sh, 1412m, 1219m, 1063m, 1040w, 1017w, 1003m, 912w, 827w, 756m, 748sh, 724w, 690w, 605s cm^{-1}.

Tris(pyridine)zinctetracarbonyliron, $(py)_3ZnFe(CO)_4$. The compound $(NH_3)_3ZnFe(CO)_4$, prepared as previously described,[4,8] was dissolved in an excess of deoxygenated pyridine under nitrogen. After evolution of NH_3 was complete, a nitrogen flow was passed over the solution for one hour. Addition of ten volumes of pentane produced an oil, which solidified on cooling to -20°C. The supernatant was removed, and the yellow-brown solid crushed to a powder. After washing with three 30 ml portions of diethylether, a bright yellow solid remained, which was dried in vacuo one hour.

Anal. Calcd. for $C_{19}H_{15}FeN_3O_4Zn$: C, 48.50; H, 3.21; N, 8.93. Found: C, 48.50; H, 3.20; N, 8.33.

Complete infrared data (Nujol mull): 1974s, 1954s, 1879s, vbr, 1821s, vbr, 1796sh, 1603m, 1485sh, 1445sh, 1213m, 1153m, 1064m, 1036m, 1006m, 752m, 693s, 618s cm^{-1}.

<u>(Ammine)(2,2'-bipyridyl)zinctetracarbonyliron, $(NH_3)(2,2'-bpy)$-$ZnFe(CO)_4$.</u> To 50 ml aqueous ammonia was added 1.3 ml (0.01 mole) of $Fe(CO)_5$ under nitrogen. After allowing this mixture to stir overnight (producing $HFe(CO)_4^-$),[4] 50 ml of a deoxygenated aqueous solution containing 2.20 grams (0.01 mole) of zinc acetate dihydrate and 1.56 grams (0.01 mole) of 2,2'-bipyridyl was added at 0° C, causing a red-violet solid to appear. After one hour, the supernatant was removed and the solid was washed with three 30 ml portions of water, followed by three 30 ml portions of diethylether. The slightly air-sensitive product was then dried <u>in vacuo</u> one hour.

Anal. Calcd. for $C_{14}H_{11}FeN_3O_4Zn$: C, 41.37; H, 2.73; N, 10.34. Found: C, 40.53; H, 2.63; N, 9.85.

Complete infrared data (Nujol mull): 3367m, 3346m, 3276w, 1975m, 1947s, 1914m, 1832s, vbr, 1788s, br, 1605m, 1596m, 1491sh, 1443sh, 1315m, 1204m, 1173w, 1157m, 1036w, 1020m, 1012sh, 834w, br, 760s, 726m, 643m, 625s cm^{-1}.

<u>(2,2'-bipyridyl)zinctetracarbonyliron, $(2,2'-bpy)ZnFe(CO)_4$.</u> By maintaining $(NH_3)(2,2'-bpy)ZnFe(CO)_4$ at 75° <u>in vacuo</u> for three days, the

desired compound, of red-violet color, was obtained.

Anal. Calcd. for $C_{14}H_8FeN_2O_4Zn$: C, 43.18; H, 2.07; N, 7.19. Found: C, 43.52; H, 2.28; N, 7.07.

Complete infrared data (Nujol mull): 2031w, 1975s, 1914s, 1881sh, 1866s, 1605m, 1597m, 1440sh, 1321m, 1258w, 1244w, 1172m, 1158m, 1060w, 1041m, 1015m, 1006sh, 760s, 727m, 715sh, 644m, 623s, 615sh cm^{-1}.

Silvertetracarbonylcobalt, $AgCo(CO)_4$. This was prepared by a variation of the method of Schubert,[14] wherein an ammoniacal aqueous $AgNO_3$ solution is reacted with aqueous $NaCo(CO)_4$[15] under nitrogen. The yellow precipitate was then filtered, washed with pentane to remove Co_2-$(CO)_8$, taken up in acetone, and filtered through a fine frit (to remove metallic silver). Addition of water to the filtrate caused precipitation of the compound. If necessary, the acetone/water recrystallization was repeated several times to complete the removal of silver (which, along with $Co_2(CO)_8$ causes rapid catalytic decomposition of the compound).[7,15] After removal of the supernatant, the solid compound was further washed with pentane, dried quickly (1 hr.) in vacuo, and stored in darkness at -20°C to avoid decomposition.

Infrared data (Nujol mull): 2069s, 2034s, 2008s, 1993s, 1961s, br, 1937s cm^{-1}.

(2, 2'-bipyridyl)silvertetracarbonylcobalt, $(2,2'-bpy)AgCo(CO)_4$. This compound was prepared by a modification of the procedure of Hieber,

et al.[8,16]   The addition of 0.46 grams (2.95 mmole) of 2,2'bipyridyl

to a freshly prepared solution of $AgCo(CO)_4$ in ethanol (from the addition

of 0.57 grams (2.95 mmole)of $NaCo(CO)_4$ in 30 ml ethanol to 0.50 grams

(2.95 mmole)of $AgNO_3$ in 30 ml ethanol) produced the desired compound.

After stirring the mixture under nitrogen for 30 minutes, the solvent

was removed in vacuo. The compound was then quickly extracted with

a large volume of methylene chloride and the resulting solution was

filtered, and reduced in volume under high vacuum. Addition of several

volumes of pentane at -20° C resulted in precipitation of the compound as

a bright yellow solid.

Anal. Calcd. for $C_{14}H_8AgCoN_2O_4$: C, 38.65; H, 1.85; N, 6.44.

Found: C, 37.67; H, 1.80; N, 6.17.

Complete infrared data (Nujol mull): 2014s, 1967s, 1938s, 1910s,

1595sh, 1590m, 1566w, 1483sh, 1473sh, 1435sh, 1314m, 1303w, 1252w,

1240w, 1204w, 1169m, 1152m, 1097w, 1055w, 1036w, 1004m, 999sh, 747s,

730m, 635mw, 613w cm^{-1}.

Spectroscopic Studies. Infrared spectra were recorded with a Perkin

Elmer 267 spectrophotometer. Mulls were prepared in a glove box with

dry, degassed Nujol. Solutions were prepared in Schlenk apparatus and

were transferred to matched NaCl cells as described previously.[17] All

spectra were calibrated with polystyrene.

X-Ray Powder Diffraction Studies. X-ray powder diffraction patterns

were recorded photographically on a Picker 6147 x-ray diffractometer

using filtered CuK_α radiation. Samples were sealed in 0.5 mm glass capillaries under nitrogen and rotated during exposure.

Unit Cell and Space Group Determination of bis(pyridine)cadmium-tetracarbonyliron, $(py)_2CdFe(CO)_4$. The compound was crystallized by very slow cooling of a hot saturated solution in pyridine/mesitylene (1:4), yielding large, well formed crystals. Elemental analysis of the single crystals proved them to be identical with the starting compound.[18]

A suitable single crystal was mounted under nitrogen in a glass capillary. Microscopic examination revealed no evidence of twinning. Oscillation, Weissenberg, and Precession photographs, using filtered $CuK\alpha$ or $MoK\alpha$ radiation revealed an orthorhombic unit cell, $\underline{a}$ = 12.42 Å, $\underline{b}$ = 22.62Å, $\underline{c}$ = 17.04Å, V = 4788Å^3. Systematic absences were observed for reflections of the type hk0, h+k odd; h0ℓ, ℓ odd; 0kℓ, k odd. These absences are uniquely consistent with space group #60, D_{2h}^{14} -Pbcn.[19] The observed density, 1.82 g/cc in a 1,4-dibromobutane/methylene bromide mixture agrees with the calculated value of 1.82g/cc for Z = 12. Since there are eight general positions in the unit cell, this means that, barring the unlikelihood of extreme disorder, the unit cell contains four trimeric units, which lie on two-fold axes (e.g., along 0, y, $\frac{1}{4}$).
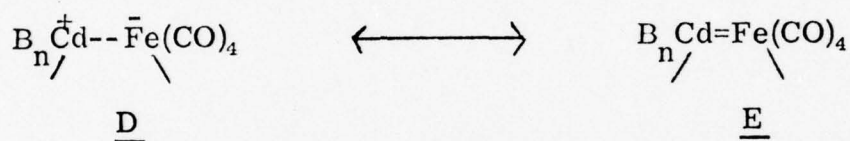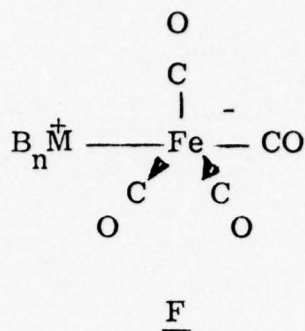
RESULTS

Group IIB Compounds

Previously reported group IIb metal-tetracarbonyliron complexes have been of the types $MFe(CO)_4$ where M = Cd[3], Hg[6,7]; $B_2MFe(CO)_4$ where M = Cd and B = NH_3[3], pyridine[3], γ - picoline[4], B_2 = 2, 2'-bipyridyl[4], 1, 10-phenanthroline[4], ethylenediamine[4]; as well as $B_3MFe(CO)_4$ where M = Zn and B = NH_3[7]. The scope of complexes which can be synthesized is expanded in the present work. By carefully controlling the stoichiometry, reaction conditions, and the nature of the ligands, we have obtained the following new types of compounds: $BCdFe(CO)_4$, from a low temperature reaction of B = $4-C_6H_5C_5H_4N$ with excess $CdFe(CO)_4$; $(4, 4'-bpy)CdFe(CO)_4$, which may be polymeric by virtue of bridging nitrogenous ligands; $B_3CdFe(CO)_4$, by using the tridentate ligand 2, 2': 6', 2''-terpyridyl (tpy); possibly $B_4CdFe(CO)_4$ by using the potentially tetradentate ligand 2, 2', 2''-triaminotriethylamine (tren);[20] and finally, $B_2ZnFe(CO)_4$ by careful removal of NH_3 from $(NH_3)(2, 2'-bpy)ZnFe(CO)_4$ _in vacuo_. Attempts to stabilize the $B_4CdFe(CO)_4$ species $(2, 2'-bpy)_2CdFe(CO)_4$ by coordination of the base on cadmium prior to reaction with $HFe(CO)_4^-$ lead simply to loss of the excess base and isolation of $[(2, 2'-bpy)CdFe(CO)_4]_3$. Attempts to prepare base adducts of $HgFe(CO)_4$ using mono- or bidentate nitrogen donor ligands also failed, as determined by x-ray powder diffraction, infrared spectroscopy, and elemental analysis. Synthetic procedures and analytical data are compiled in the Experimental Section.

From our previous work in group IIb[5,21] and group IVb[22,23] metal-transition metal chemistry as well from established electron density - CO force constant relationships in metal carbonyl vibrational spectroscopy[5,24], it is possible to draw a number of qualitative structural inferences about the new $Fe(CO)_4$ derivatives from band positions, splittings and intensities in the infrared spectra. In particular, progressive coordination of Lewis base molecules to the main group metal is expected to weaken or destroy metal-metal bonding[5,23,25]. Furthermore, the accompanying base stabilization of ionic resonance hybrids such as $\underline{D}$ is predicted to

$$B_n\overset{+}{C}d\text{-}\text{-}\overset{-}{F}e(CO)_4 \qquad \longleftrightarrow \qquad B_nCd=Fe(CO)_4$$

$$\underline{D} \qquad\qquad\qquad\qquad\qquad \underline{E}$$

result in a lowering of C-O stretching frequencies due to increased population of C-O π^* orbitals and decreased C-O bond order. Whether a particular $B_nMFe(CO)_4$ species is or is not oligomeric can be investigated by comparing spectra in the solid state[24f] or in noncoordinating solvents with those obtained in coordinating solvents (e.g. pyridine). Base-induced metal-metal bond fracture by the coordinating solvent will result in a shift of the νC-O absorptions to lower energy. Upon full cleavage to bimetallic units, the band pattern generally simplifies and is characteristic of the C_{3v} local symmetry ($2A_1$; 1E modes) monomer, $\underline{F}$[5].

$$\begin{array}{c} O \\ \| \\ C \\ | \\ B_n\overset{+}{M}\!\!-\!\!-\!\!-\!\!\overset{-}{Fe}\!\!-\!\!CO \\ C \quad C \\ \| \quad \| \\ O \quad O \end{array}$$

<u>F</u>

Such structures have been identified for isoelectronic $R_2(B)M'Fe(CO)_4$[23,25a] and $X_3M'Fe(CO)_4^-$[26] derivatives (M' = group IVb metal), $(py)_3CdFe(CO)_4$ (shown to be monomeric in solution)[5], $HFe(CO)_4^-$[27], and $RFe(CO)_4^-$ ($R = n\text{-}C_3H_7$)[28]. Cleavage of all metal-metal bonds to yield an ionic structure, <u>A</u>, would displace the C-O vibrational frequencies to the region of $Na_2Fe(CO)_4$, i.e. 1720 cm^{-1} in $[(cryptate)Na]_2Fe(CO)_4$,[28a] 1730 cm^{-1} in DMF,[29] and 1761 cm^{-1} as a Nujol mull.[27] As will be seen, the above vibrational spectroscopic information can be supplemented by x-ray powder diffraction studies in the solid and molecular weight measurements in solution. Detailed metrical data, however, will only come from complete single crystal diffraction studies.

Solid state infrared spectra in the C-O stretching region of representative group IIb metal-transition metal derivatives are shown in Figure 2. Numerical data are summarized in Table I along with solution molecular weights. It can be seen that increasing the number as well as the basicity of donor molecules coordinated to the group IIb metal generally leads to

a lowering of the carbonyl stretching frequencies. Also, zinc complexes have lower energy C-O stretching transitions than cadmium analogues. These trends reflect increasing polarity of metal-metal bonding and negative charge build-up on the $Fe(CO)_4$ fragment. The lowest C-O stretching frequencies are observed for the $B_3M Fe(CO)_4$ complexes. The energies of the carbonyl stretching absorptions in the latter compounds shift very little on dissolution in coordinating solvents. Furthermore, solution spectra (Figure 3) are in good agreement with the approximately C_{3v} structure F.[5,24] These observations viewed in light of the molecular weight data and the saturation of the M^{+2} coordination sphere strongly suggest monomeric structures[30]. The complex $(tren)CdFe(CO)_4$ possesses the lowest energy ν_{C-O} absorptions of any of the molecules examined. Though the energies and the molecular symmetry as revealed by the band multiplicity are not compatible with a purely ionic structure, it appears that tetradentate Cd^{+2} coordination by the tren ligand may be placing additional negative charge on the tetracarbonyliron moiety. In none of the compounds studied was the characteristic C-O band position of an isocarbonyl species[31], G, observed. A strong transition in

$$Fe-C \equiv O \nearrow M^{+2}$$

G
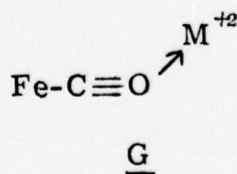
the infrared spectrum of (tren)CdFe(CO)$_4$ at 1583 cm^{-1} can be assigned to an NH$_2$ deformation[32]; in the free ligand this band occurs at 1592 cm^{-1}.

The B$_2$MFe(CO)$_4$ molecules all appear to be associated to some degree. We have already shown (2, 2'-bpy)CdFe(CO)$_4$ to be trimeric in the solid state and in noncoordinating solvents[5]. The space group and unit cell parameters of (py)$_2$CdFe(CO)$_4$ also suggest a trimeric structure in the crystal (see Experimental Section for details). On the basis of infrared spectral and molecular weight studies, this compound is known to exist in pyridine solution as monomeric (py)$_3$CdFe(CO)$_4$[5a]. X-ray powder diffraction studies revealed that (2, 2'-bpy)ZnFe(CO)$_4$ and (2, 2'-bpy)Cd-Fe(CO)$_4$ are not isomorphous. The exact structure of the Zn compound remains undetermined, however the similarity of the ν_{C-O} multiplicities and energies to those of the Cd analogue strongly suggest an associated structure. This compound is insufficiently soluble for solution molecular weight determination. The BCdFe(CO)$_4$ compound (4-C$_6$H$_5$C$_5$H$_4$N)CdFe(CO)$_4$ is found to be dimeric in benzene (Table I). Though a similar structure could be adopted by (4, 4-bpy)CdFe(CO)$_4$, the very low solubility of this complex along with the lower C-O stretching frequencies suggests an oligomeric bpy cross-linked structure with both nitrogen atoms involved in Cd^{+2} coordination (to different cadmium ions).

Silver and Lead Complexes

A number of structural similarities exist between isoelectronic pairs of group IIb and group IVb metal-transition metal complexes. For
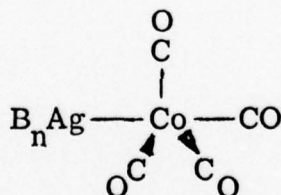
example, the $B_3MFe(CO)_4$ and $R_2(B)M'Fe(CO)_4$[23,25a] (M'=Si, Ge, Sn, Pb) compounds are largely monomeric, while $B_2CdFe(CO)_4$ and $R_2M'Fe(CO)_4$[33] compounds appear, in the absence of overwhelming steric factors, to be associated. These similarities motivated the examination of relationships among similar compounds involving group IVb (divalent), group IIIb, and group Ib metal ions. For example, the structures of $AgCo(CO)_4$[14] and $PbFe(CO)_4$[9] are unknown, while those of their respective isoelectronic analogs, $[CdFe(CO)_4]_4$[5a] and $TlCo(CO)_4$[12] (largely ionic structure)[12a] are known. The solid state infrared spectra of $PbFe(CO)_4$ and $TlCo(CO)_4$ are compared in Figure 2, and are seen to be rather dissimilar. The spectrum of $PbFe(CO)_4$ resembles that of an oligomeric structure, i.e. the bands are shifted very much to high frequency, coming near those of $CdFe(CO)_4$ and $Fe(CO)_4Cl_2$ (Table I), whereas the spectrum of the more ionic $TlCo(CO)_4$ is reasonably close to that of $NaCo(CO)_4$ (Table I, Figure 2). In agreement with these observations, x-ray powder patterns reveal that these compounds are not isomorphous. Efforts to cleave $PbFe(CO)_4$ with a variety of Lewis bases were unsuccessful.

In contrast to the Pb, Tl results, the infrared spectra of $AgCo(CO)_4$ and $[CdFe(CO)_4]_4$ are qualitatively rather similar (Figure 2), although the C-O stretching transitions of $AgCo(CO)_4$ occur at somewhat higher energy, in accord with the lower formal negative charge on the $Co(CO)_4^-$ fragment as compared to the $Fe(CO)_4^{2-}$ fragment[24]. This result suggests that the

compounds may be composed of similar oligomeric units. Indeed, x-ray powder powder diffraction diffraction data (Table II) show them to be isomorphous. Thus, in $AgCo(CO)_4$, the metal atoms are also arrayed in an approximately planar, centrosymmetric eight-membered ring. Unlike $[CdFe(CO)_4]_4$, $[AgCo(CO)_4]_4$ is particularly prone to thermal decomposition, yielding Ag and $Co_2(CO)_8$. The decomposition is catalyzed so greatly by even traces of Ag that various attempts to crystallize the compound by a reversible homolytic metal-metal bond cleavage cycle have so far been fruitless.

The compounds $(2,2'\text{-bpy})AgCo(CO)_4$ and $[(2,2'\text{-bpy})CdFe(CO)_4]_3$ were also investigated for a possible structural relationship. The Nujol mull and solution infrared spectra of these compounds (Table I and Figure 3) are not particularly similar, and the solid compounds, each recrystallized from CH_2Cl_2/hexane, are not isomorphous by x-ray powder diffraction. The infrared spectrum of $(2,2'\text{-bpy})AgCo(CO)_4$ in CH_2Cl_2 (Figure 3) is essentially that expected for a monomeric C_{3V} structure such as $\underline{H}$.[24,34] Furthermore, the compound is found to be

$$
\begin{array}{c}
O \\
\parallel \\
C \\
| \\
B_nAg \!-\!-\! Co \!-\!-\! CO \\
\end{array}
$$

$$
\underset{O}{\overset{C}{\diagup}} \quad \underset{O}{\overset{C}{\diagdown}}
$$

$\underline{H}$

only partially associated in methylene chloride solution by osmometry. Relatively small shifts of the C-O stretching transitions are observed in pyridine

solution (Table I, Figure 3) indicating a similar structure with possible weak coordination of an additional molecule of base. The related compound (o-triars)AgCo(CO)$_4$ (o-triars=bis(o-dimethylarsinophenyl)methyl-arsine) is known to be monomeric in solution and exhibits a similar infrared spectrum[35] (Table I).

DISCUSSION

The results of these studies have shown that $B_nMFe(CO)_4$ complexes (for M = Zn or Cd) other than those normally favored by typical mono-dentate ligands in the solid state can be isolated using an appropriate ligational strategy. Thus, not only have solution-state structures (e.g., monomeric $B_3CdFe(CO)_4$[5]) been stabilized in the solid state, but structures previously unknown in either phase have been obtained (e.g., $B_2ZnFe(CO)_4$ and $BCdFe(CO)_4$). The solid state structures of these and isoelectronic species thus far observed fall into three categories of aggregation: ionic (A), monomeric (B), and oligomeric (C). Through this series the iron coordination number ranges from four to six. The ionic extreme has already been established in $[(cryptate)Na]_2Fe(CO)_4$[36] as well as in iso-electronic $TlCo(CO)_4$,[12] while $(B)R_2M'Fe(CO)_4$,[23,25a] $B_3CdFe(CO)_4$,[5] and (o-triars)AgCo(CO)$_4$[35] are known to be monomeric. Similarly, oli-gomeric structures have been demonstrated for $[CdFe(CO)_4]_4$,[5] $B_2CdFe(CO)_4$,[5] and $R_2M'Fe(CO)_4$ species[33] with normal R groups. The present studies

have shown that $B_2ZnFe(CO)_4$ ($B_2 = 2,2'$-bpy), $BCdFe(CO)_4$ ($B = 4$-$C_6H_5C_5$-H_4N), and $AgCo(CO)_4$ are most likely oligomeric, while $B_3ZnFe(CO)_4$ ($B = $ py, $(NH_3)(2,2'$-bpy)), $B_nAgCo(CO)_4$($B_n = (2,2'$-bpy)), and $B_3CdFe(CO)_4$ ($B_3 = $ tpy, tren) are most likely monomeric, or only very weakly associated.

Two key factors in determining which structure is favored for a given complex seem to be the formal positive charge on, and the electronegativity of, the main group metal. For example, in comparing the isoelectronic $B_2AgCo(CO)_4$ and $B_2CdFe(CO)_4$ complexes, the oligomeric nature of the latter species plausibly derives from the greater difficulty in separating ions of formal charge ± 2 as compared to ± 1 in the former complexes. Within group IIb, the most common compounds of zinc are monomeric with three base molecules ($B_3ZnFe(CO)_4$) and those of cadmium are oligomeric in the solid state with two base molecules ($B_2CdFe(CO)_4$), while $HgFe(CO)_4$ does not form base adducts. This trend reflects the propensity of the harder and more acidic main group metals to be coordinated by the nitrogen donor ligands, which are harder than the $Fe(CO)_4$ moiety. Alternatively, it could be said that zinc, being the most electropositive group IIb metal, is best capable of stabilizing the positive charge resulting from resonance hybrid $\underline{I}$. Species of the type $B_3CdFe(CO)_4$ are

$$
\begin{array}{c}
B_{\searrow}^+ \\
^{\searrow}Zn\!-\!\bar{F}e(CO)_4 \\
B^{\nearrow\uparrow} \\
B
\end{array}
$$

$$\underline{I}$$
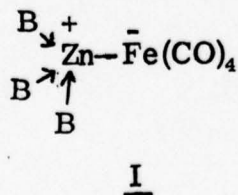
generally observed only when very large excesses of B are present (e.g. in

pyridine solutions). However, even though zinc displays a strong prefer-
ence for bonding to the harder nitrogen donors in monomeric complexes,
we have prepared the $(2,2'bpy)ZnFe(CO)_4$ oligomer from the $(NH_3)(2,2'-bpy)ZnFe(CO)_4$ monomer by taking advantage of the greater volatility of
NH_3. Our inability to isolate base adducts of $HgFe(CO)_4$
parallels previous work on $M[Co(CO)_4]_2$ compounds (M = Zn, Cd, Hg).[37]
The marked tendency for mercury to retain two-coordination has often
been attributed to a high 6s - 6p promotional energy.[38]

After considering the factors which control stoichiometry and the
extent of association of the complexes, it is next appropriate to discuss
the extent of oligomerization in some of the specific cases. From the
unit cell and space group determination of $(py)_2CdFe(CO)_4$ (see Experi-
mental Section), we have found that this complex is trimeric in the solid
state, as in the case of the related 2,2'-bipyridyl complex[5b]. In contrast,
the isoelectronic $R_2SnFe(CO)_4$ compounds are dimeric[33] (Structure J). The
trimeric structures of $(2,2'-bpy)CdFe(CO)_4$ and $(py)_2CdFe(CO)_4$

J
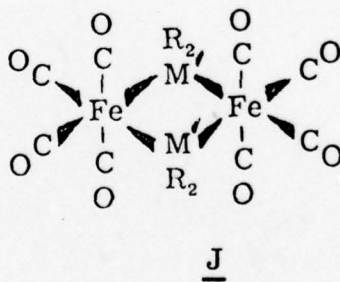
appear to reflect the preferred valence angles at the group IIb metal and at iron. The Fe-Cd-Fe angles in the bipyridyl complex are in the range 138.81(15)° - 148.40(15)°,[5b] while the Fe-Sn-Fe angles in $[(CH_3)_2SnFe(CO)_4]_2$[33b] are 103.**7**(4)° and 102.6(3)°, and in $[(\eta'-C_5H_5)_2SnFe(CO)_4]_2$[33a] are 102.04(3)°. The larger angles in the Cd compound seem to reflect a preference for greater cadmium s character in the more covalent Cd-Fe bonds (as opposed to the weaker Cd-N coordinate bonds), while in the group IVb system the Sn-C and Sn-Fe bonds are more equal in covalency and the hybridization is expected to be more near tetrahedral. It should be noted, in support of relatively constant cadmium hybridization, that in the series $B_nCd[Mn(CO)_5]_2$, B = terpyridyl,[39a] diglyme,[39b] 2,2'-bipyridyl,[39c] and 1,10-phenanthroline[39c], the observed Mn-Cd-Mn angles are in the relatively narrow range of 128-136°. The larger Fe-Cd-Fe angles in $B_2CdFe(CO)_4$ species clearly favor a ring size larger than 4 members. In addition to factors involving the main group metal ion, it was noted in the discussion of the $[(2,2'-bpy)CdFe(CO)_4]_3$ structure[5b] that the tetracarbonyliron coordination geometry was appreciably distorted from octahedral toward bicapped tetrahedral (the two cadmium atoms located at the capping vertices), with Cd-Fe-Cd angles ranging from 94.9(1)° to 102.2(2)° and C_{axial}-Fe-C_{axial} angles of 135.8(15)°- 141.8(15)°. This distortion was attributed to the large amount of electron density being released by the cadmium atom onto the $Fe(CO)_4$ fragment. Such a distortion also destabilizes a 4-membered ring both because the Cd-Fe-Cd angles would be too large and because close non-bonded contacts (~2Å)

are predicted betweed axial carbonyl ligands on opposite iron atoms.

In contrast, Sn-Fe-Sn angles in the two aforementioned group IVb compounds were reported to be 76.3(4)°, 77.4(3)°;[33b] and 77.96(2)°,[33a] respectively. This contraction from the octahedral 90°[40] is clearly more compatible with a 4-membered ring. Not surprisingly, infrared spectra in the C-O stretching region reveal less electron density on the iron in the group IVb than in the group IIb compounds[5]. That the new group IIb compound $[(4-C_6H_5C_5H_4N)CdFe(CO)_4]_2$ is apparently dimeric in solution suggests that, to maintain a planar ring structure, the tetra-carbonyliron valence angles must decrease markedly in response to the removal of a base molecule from cadmium, while the Fe-Cd-Fe angles must decrease to less than 120°. A solid state structure determination for this compound would clearly be of interest.

Isoelectronic Relationships

In our studies on the two isoelectronic pairs, $TlCo(CO)_4$ and $PbFe(CO)_4$, and $AgCo(CO)_4$ and $CdFe(CO)_4$, the conclusions drawn on the basis of infrared spectroscopy and x-ray powder diffraction parallel other known relationships. Thus, the first pair are as different in their chemical and physical properties as they are in their spectroscopic ones. While $TlCo(CO)_4$ is yellow, sublimable, and soluble in aromatic solvents,[12] $PbFe(CO)_4$ is black, non-sublimable, insoluble in aromatic solvents, and only very slightly soluble in coordinating solvents.[9] Both are very air-sensitive, however. In this case, the chemical and physical differences

are probably related to the fact that while Pb(II) tends toward high coordination numbers involving a stereochemically active (hence, nonbonding) lone pair,[41] in Tl(I) the lone pair (at or near room temperature, at least) is essentially spherical, and hence metal-to-ligand sigma antibonding which, along with the lower formal charge on thallium, tends to reduce the tendency to high coordination numbers.[42]

The structural similarities of the second isoelectronic pair, $AgCo(CO)_4$ and $CdFe(CO)_4$ (both planar tetramers) fall in line with other chemical similarities. Both compounds are yellow, nonvolatile, soluble in coordinating solvents (e.g., acetone) from which they can be precipitated by the addition of water (cf., reversible homolytic cleavage cycle),[5,23a] and form bipyridyl adducts. The chemical similarities in this case seem to stem from the ability of the two isoelectronic main group metals, Ag(I) and Cd(II), to adopt either linear, two-coordinate sp complexes, or higher (especially three or four) coordination numbers.[43] However, the formal difference in charge does manifest itself in the 2,2'-bipyridyl adducts, where the cadmium complex is oligomeric while the silver complex is only partially associated. It can also be noted that while many cis-octahedral $Fe(CO)_4X_2$ complexes are known,[40] $[AgCo(CO)_4]_4$ appears to be the first such cobalt complex.

While $AgCo(CO)_4$ and $CdFe(CO)_4$ are isoelectronic and isostructural, some interesting differences do exist in their available resonance hybrids.

Those of $CdFe(CO)_4$ and its base adducts involve (neglecting ligands):

$$\overset{}{\underset{}{Cd}}-\overset{}{\underset{}{Fe}} \longleftrightarrow \overset{+}{\underset{}{Cd}} \quad \overset{-}{\underset{}{Fe}}, \quad \overset{+}{Cd}-\overset{-}{Fe} \longleftrightarrow \overset{2+}{Cd} \quad \overset{2-}{Fe}$$
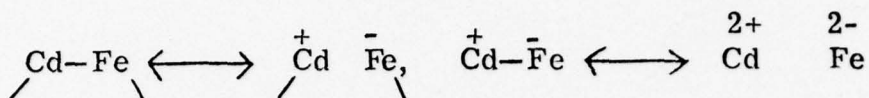
while the corresponding resonance structures for $AgCo(CO)_4$ and its base adducts are

$$\overset{-}{\underset{}{Ag}}-\overset{+}{\underset{}{Co}} \longleftrightarrow Ag \quad Co, \quad Ag-Co \longleftrightarrow \overset{+}{Ag} \quad \overset{-}{Co}$$
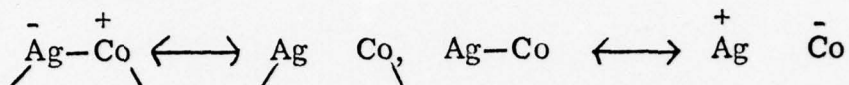
For the silver-cobalt system, a much more convenient resonance formalism can be adopted, utilizing donation of lone pairs of electrons from the transition metal carbonyl to the main group metal. This is known in the related compounds $(C_5H_5)Co(CO)_2 \cdot HgCl_2$,[44a], $(C_5H_5)Co$-(olefin)$_2 \cdot HgCl_2$,[44a] $(C_5H_5)Rh(olefin)_2 \cdot HgCl_2$,[44a] $Fe(CO)_5 \cdot HgCl_2$,[44b] $[(C_6H_5)(CH_3)_2P]_2Fe(CO)_3 \cdot HgCl_2$[44c] as well as others.[44d-h] Thus, $H:\overset{H}{\overset{..}{Fe}}(CO)_4$, in forming the dianion, clearly has at least two electron pairs available, as does the isoelectronic $Co(CO)_4^-$. Resonance structures ($\underline{K}$) and ($\underline{L}$) (neglecting ligands) can then be invoked in which the extent of lone pair donation is variable.

$$\overset{+}{Ag} \longleftarrow \overset{-}{Co}$$
$$\underline{K}$$
oligomer

$$\overset{+}{Ag} \longleftarrow \overset{-}{Co}$$
$$\underline{L}$$
monomer
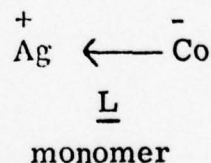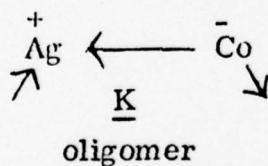
Concluding Remarks

In our synthetic, spectroscopic, and crystallographic studies on $B_nMFe(CO)_4$ and $B_nM'Co(CO)_4$ type compounds, we have found that the

main group metal with attendant ligands plays a dominant role in determining the type of structure adopted and the resulting chemical and physical properties. Besides determining its own coordination sphere and tendency to form base adducts, the main group metal is primarily responsible for the extent of cation/anion association in these compounds, which encompasses ionic, monomeric, oligomeric, and possibly (but not presently) isocarbonyl structures. By suitable adaptation of the main group metal and the ligands chosen, we have shown that otherwise unfavored structures for a particular metal can be stabilized, thus potentially allowing for more detailed analysis of formerly unstable or solution-state structures. Such manipulations could also result in preferential stabilization of infinite metal chains, and will be the subject of future investigations.

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    b. It is recognized that the coplanarity of the three nitrogen atom donors in 2,2':6',2"-terpyridyl means that the Cd^{+2} ion coordinative saturation is not as extensive as in the B_3 complexes with monodentate bases. Thus a possibility for oligomerization does exist,[39a] but such a situation is not unambiguously indicated in the infrared spectra of $(tpy)CdFe(CO)_4$.

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TABLE I.

Comparison of Infrared-Active C–O Stretching Frequencies in Related Metal Carbonyl Complexes[a]

Compound	Phase	νCO, cm^{-1}	Molecular[b] Weight	Solvent
[CdFe(CO)$_4$]$_4$	Nujol mull	2032s, 2012m, 1972ms, 1961ms, 1946m, 1920s,br 1867s, br, 1840w, sh		
PbFe(CO)$_4$	Nujol mull	2049s, 2006m, 1990w, sh 1978w, sh, 1964ms		
[(4-C$_5$H$_5$C$_5$H$_4$)CdFe(CO)$_4$]$_2$	Nujol mull	2000s, 1990sh, 1941sh, 1933sh, 1914s, 1907sh, 1891s, 1868sh, 1840m, 1806m		
[(4-C$_6$H$_5$C$_5$H$_4$N)CdFe(CO)$_4$]$_2$	CH$_2$Cl$_2$	1992m, 1927s, br	819(873)	benzene
[(2,2'-bpy)CdFe(CO)$_4$]$_3$[c]	benzene	1982vs, 1922s, 1894ms, 1879sh	1344(1308)	benzene
(py)$_3$CdFe(CO)$_4$[c]	pyridine	1976s, 1908vs, 1886sh	320(280)[c]	pyridine
(tpy)CdFe(CO)$_4$	Nujol mull	1985sh, 1973s, 1887s, 1872sh, 1850sh		
(tpy)CdFe(CO)$_4$	pyridine	1977s, 1907vs, 1888sh		
(tren)CdFe(CO)$_4$	Nujol mull	1948s, 1857s, 1815sh 1798vs, br		

TABLE I continued

Compound	Phase	νCO, cm^{-1}	Molecular[b] Weight	Solvent
(4, 4'- bpy)CdFe(CO)$_4$	Nujol mull	1977s, 1904s, 1892s, sh		
(2, 2'- bpy)ZnFe(CO)$_4$	Nujol mull	1975s, 1914s, 1881sh, 1866s		
(NH$_3$)(2, 2'- bipy)ZnFe(CO)$_4$	Nujol mull	1975m, 1947s, 1914m 1832s, 1788s		
(NH$_3$)$_3$ZnFe(CO)$_4$	Nujol mull	1994m, 1943s		
(py)$_5$ZnFe(CO)$_4$	Nujol mull	1974s, 1954s, 1879s, br, 1821s, 1796sh		
(py)$_3$ZnFe(CO)$_4$	pyridine	1954ms, 1857ms, 1823s	487(470)	pyridine
[Et$_4$N]HFe(CO)$_4$[d]	Nujol mull	2008mw, 1910sh, 1848s, br		
Na$_2$Fe(CO)$_4$[24a]	Nujol mull	1761s		
Na$_2$Fe(CO)$_4$[24b]	DMF	1730s		
[(cryptateNa)$_2$Fe(CO)$_4$[e]	KBr	1720s		
Fe(CO)$_4$Cl$_2$[f]	C$_2$Cl$_4$	2164w, 2124s, 2108m, 2084s		

TABLE I continued

Compound	Phase	νCO, cm^{-1}	Molecular[b] Weight	Solvent
AgCo(CO)$_4$	Nujol mull	2069s, 2034s, 2008s 1993s, 1961s, br, 1937s		
TlCo(CO)$_4$	Nujol mull	2020mw, 1931vs, 1900m, sh	376(375)[g]	benzene[g]
(2,2'-bpy)AgCo(CO)$_4$	Nujol mull	2014s, 1967s, 1938s, 1910s		
(2,2'-bpy)AgCo(CO)$_4$	CH$_2$Cl$_2$	2023ms, 1954sh, 1940s, br	603(435)	
(2,2'-bpy)AgCo(CO)$_4$	pyridine	2011ms, 1930sh, 1910s, br		
(o-triars)AgCo(CO)$_4$[h]	CHCl$_3$	2037s, 1953sh, 1923s	778(730)[h]	benzene
NaCo(CO)$_4$[i]	DMF	1892s		
Co(CO)$_4$Cl[j]	acetone	2120m, 2068m, 2046s, br		

[a] m = medium; s = strong; sh = shoulder; br = broad; w = weak; v = very.

[b] Value in parenthesis is that calculated for the formula unit shown in the left-hand column.

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TABLE II

Most Prominent X-Ray Powder Diffraction Lines for

$[CdFe(CO)_4]_4$ and $AgCo(CO)_4$, mm. $(1mm/°4_\theta)$

$[CdFe(CO)_4]_4$	$AgCo(CO)_4$
18.4s	18.0s
20.4w	19.9m
29.2s	28.0s
36.6s	34.5s, 36.1mw
43.6mw	43.2m
62.1s	60.8s
--	67.1m
72.5s	72.0s

Figure 1

Perspective views of $[(2,2'\text{-bpy})CdFe(CO)_4]_3$ (from reference 5b) and $[CdFe(CO)_4]_4$, (from reference 5a).
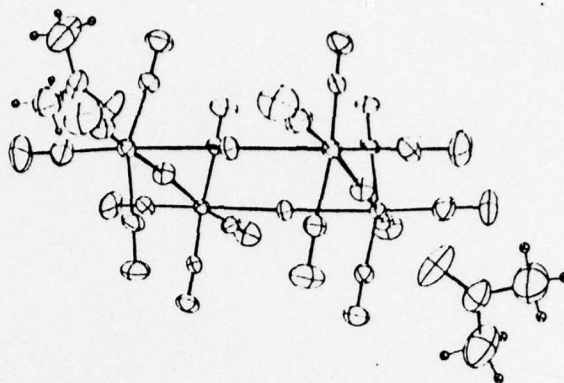
$[CdFe(CO)_4]_4$
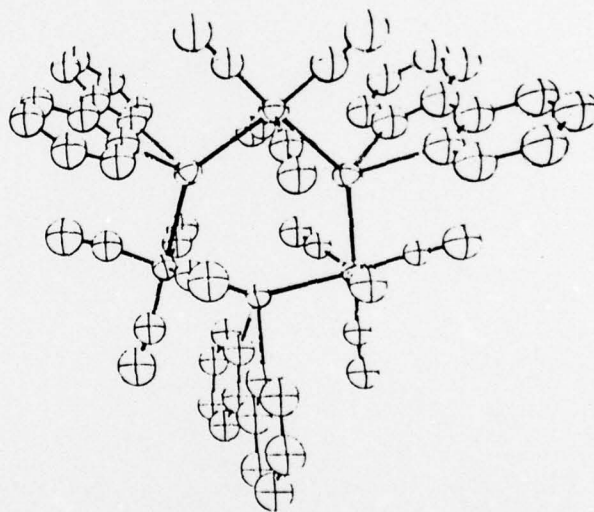
$[(bpy)CdFe(CO)_4]_3$

Figure 2

Nujol Mull Infrared Spectra of Various Metal Carbonyl Complexes.

A. $AgCo(CO)_4$

B. $TlCo(CO)_4$

C. $PbFe(CO)_4$

D. $(2,2'-bpy)ZnFe(CO)_4$

E. $(py)_3ZnFe(CO)_4$

F. $CdFe(CO)_4$

G. $(4-C_6H_5C_5H_4N)CdFe(CO)_4$

H. $(4,4'-bpy)CdFe(CO)_4$
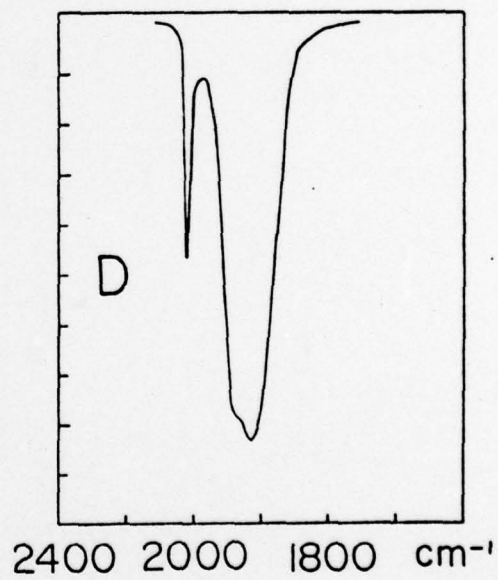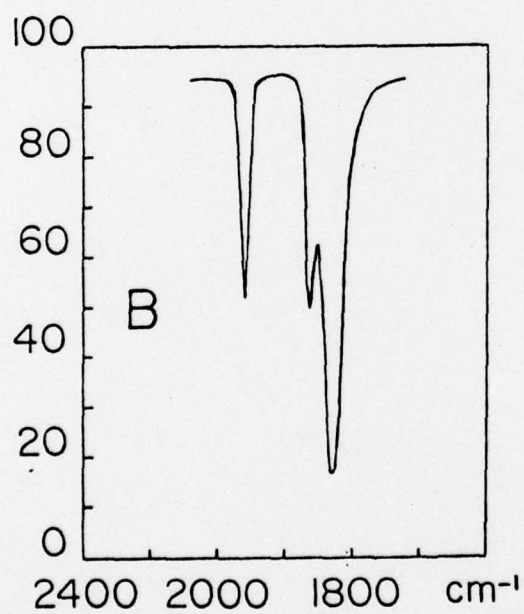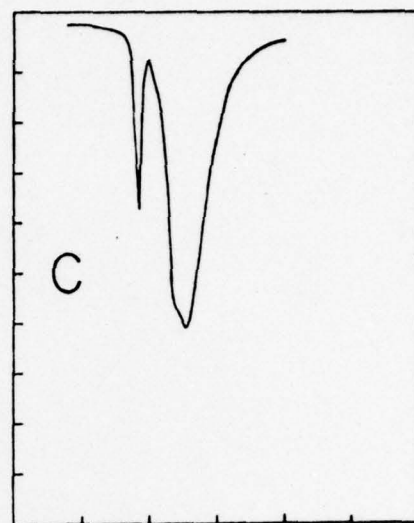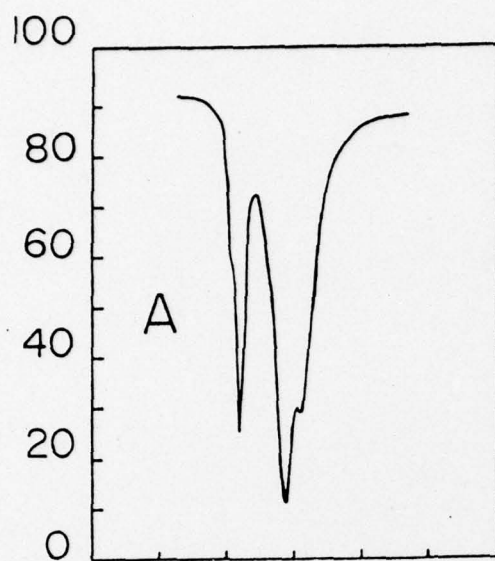
I. $(tpy)CdFe(CO)_4$

J. $(tren)CdFe(CO)_4$
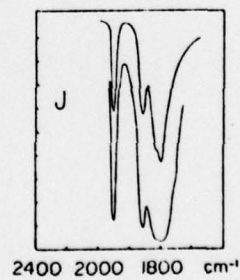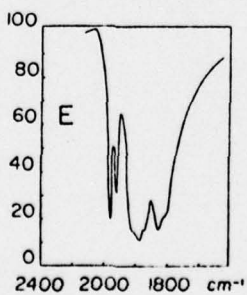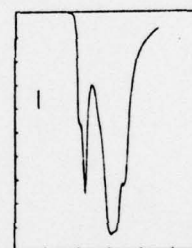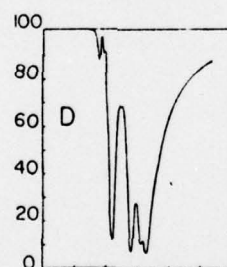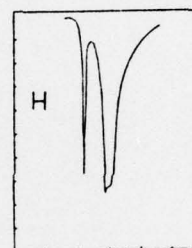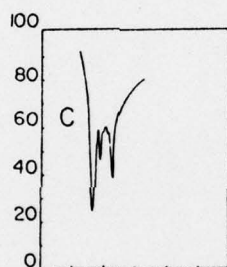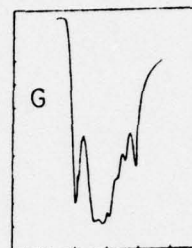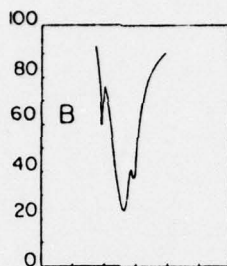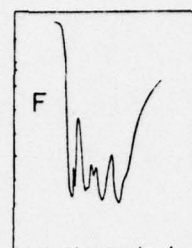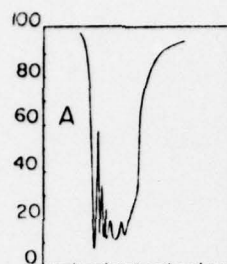
Figure 3

Solution infrared spectra for various monomeric metal-metal bonded carbonyls.

A. $(tpy)CdFe(CO)_4$ in pyridine

B. $(py)_3ZnFe(CO)_4$ in pyridine

C. $(2,2'-bpy)AgCo(CO)_4$ in CH_2Cl_2

D. $(2,2'-bpy)AgCo(CO)_4$ in pyridine

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